Laboratory Investigation of Electro-Osmotic Remediation of Fine-Grained Sediments

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LABORATORY INVESTIGATION OF ELECTRO-OSMOTIC REMEDIATION OF FINE-GRAINED SEDIMENTS

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ABSTRACT: Electro-osmosis, a coupled-flow phenomenon in which an applied electrical potential gradient drives water flow, may be used to induce water flow through fine-grained sediments. We plan to use this technology to remediate chlorinated solvent-contaminated clayey zones at the LLNL site. The electro-osmotic conductivity (k_e) determined from bench-top studies for a core extracted from a sediment zone 36.4-36.6 m below surface was initially 7.37 x 10^{-10} m^2/s-V, decreasing to 3.44 x 10^{-10} m^2/s-V, after electro-osmotically transporting 0.70 pore volumes of water through it (195 ml). Hydraulic conductivity (k_h) of the same core was initially measured to be 5.00 x 10^{-10} m/s, decreasing to 4.08 x 10^{-10} m/s at the end of processing. This decline in permeability is likely due to formation of a chemical precipitation zone within the core. Water splitting products and ions electromigrate and precipitate within the core; H^+ and metal cations migrate toward the cathode, and OH^- from the cathode moves toward the anode. We are now exploring how to minimize this effect using pH control. The significance of this technology is that for this core, a 3 V/cm voltage gradient produced an initial effective hydraulic conductivity of 2.21 x 10^{-7} m/s, >400x greater than the initial hydraulic conductivity.

INTRODUCTION

Despite on-going remediation efforts utilizing a variety of technologies, fine-grained sediments contaminated with organic solvents remain recalcitrant. These contaminated fine-grained areas are sources, slowly diffusing dissolved contaminants into adjacent high-permeability zones, leading to groundwater contamination. We are exploring the use of *in-situ* electro-osmotic pumping to flush contaminants from fine-grained sediments (Cherepy, et al., 1999).

Electro-osmotic pumping of water is a known technology with applications in structural engineering for soil stabilization (Casagrande, 1949), mining (Lockhart, 1983), and remediation (Ho, et al. 1999; Acar, et al. 1995; Lageman, 1993; Probstein and Hicks, 1993). Electromigration, electro-osmosis and electrophoresis are collectively referred to as electrokinetics (Mitchell, 1993). Electrokinetic soil remediation technology employs electrodes placed in the ground with a direct current (DC) passed between them using an external power supply. Clays have a net negative surface charge, balanced in the Helmholtz double layer by exchangeable cations. Electromigration may be used for removal of metal contaminants, such as lead and cadmium (Lageman, 1993). Electro-

osmosis is a secondary effect arising from electromigration of cations through the porous matrix under an applied electrical potential. The flow of current results in movement of the cations and their associated water of hydration from anode to cathode, entraining contaminants, if present in the pores, in the flow.

Electro-osmotic pumping can increase well yield in fine-grained sediments two to three orders of magnitude over flow rates achievable by hydraulic pumping alone. Contaminated water delivered to the cathode by electro-osmosis may then be mechanically pumped from the cathode well, and contaminants removed. The electro-osmotic conductivities of fine-grained clays with very low hydraulic conductivities (as low as 10^{-11} m/s) and of larger-grained sands with hydraulic conductivities of $\sim 10^{-6}$ m/s lie within the same narrow range, from 10^{-9} to 10^{-8} m^2/s-V. Thus, for soils with hydraulic conductivities so low that standard mechanical pump-and-treat technology is virtually ineffective, electro-osmotic pumping can greatly accelerate contaminant removal.

EXPERIMENTAL

A bench-top cell allowed us to make measurements of electrical (σ_e), hydraulic (k_h) and electro-osmotic (k_e) conductivities of a soil core. Electrical conductivity, σ_e, is determined using Ohm's Law, $\sigma_e = IL/EA$, where I is the current, L is the distance between electrodes, E is the voltage drop and A is the cross-sectional area of the core. Hydraulic conductivity, k_h, is obtained using Darcy's Law, $k_h = q_h L/HA$, where q_h is the hydraulic flux and H is the hydraulic pressure gradient. The electro-osmotic conductivity, k_e, is calculated using $k_e = q_e L/EA$, where q_e is the electro-osmotic flux.

Bench-top Cell. We have designed and built a test cell to measure electro-osmotic and hydraulic flow, electric current and voltage distributions (Cherepy, 1999). *In-situ* conditions are simulated by subjecting the sample to a confining pressure matching the underground stresses of the original location of the soil core. The core used in the measurements reported here was extracted from the 36.4-36.6 m depth of a well drilled for a field installation. In this area, the water table lies at 29 m, and the stresses on the core can thus be estimated to lie in the 0.21-0.42 MPa range. Therefore, all bench-top measurements were acquired with confining pressure of 30 psi (0.21 MPa). The test cell (Figure 1a) consists of a pressure vessel holding a 8.9 cm diameter by 15.2 cm long soil core (Figure 1b). The core is jacketed with a Teflon sleeve to seal against the confining pressure and to avoid short circuiting of the water flow at the circumference of the sample. Two perforated gold plated copper electrodes (anode and cathode) are placed on each end of the sample, and gold wire hoops placed around the core, 2 inches from each electrode, for use as voltage probes. The gold-plated diffusion plates are used to transfer the applied longitudinal load to the sample, as well as serving as electrodes. They are separated from the soil by a microporous membrane (Pall-RAI Electropore E40201ultra high MW polyethylene, 100 μm thick, 2 μm pores). A 0-50 V Hewlett-Packard 6633B power supply was employed in DC constant voltage mode for electro-osmotic conductivity measurements. Water is supplied to the anode side of the cell by a constant hydraulic head standpipe during electro-osmotic flow measurements and by a pressurized water vessel for hydraulic flow

measurements. A narrow diameter standpipe, outfitted with a 0-1.25 psi (0-8618 Pa) pressure transducer (Validyne DP 215-50), is used to measure water outflow.
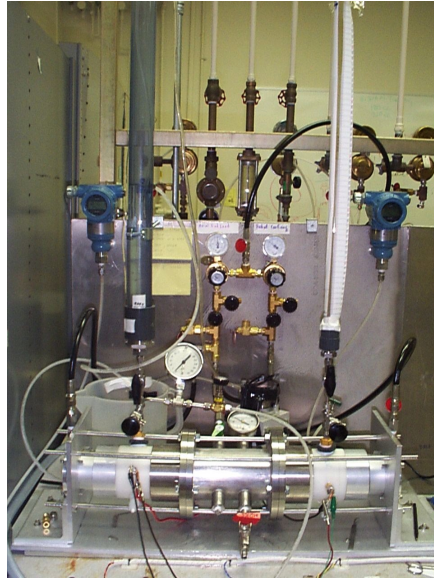

FIGURE 1A. Bench-top cell. The core is contained within the central pressure vessel, and water flow is measured as the level rises in the right hand (cathode) standpipe. For these experiments, the working electrodes were placed in direct contact with the soil.
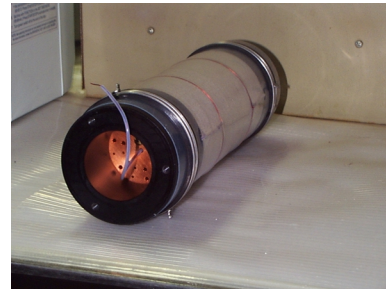

FIGURE 1B. Core assembly. The core is jacketed in Teflon shrinkwrap, with gold-plated copper perforated electrodes at both ends, and two gold hoop voltage probes to provide information about the voltage drop along the core.
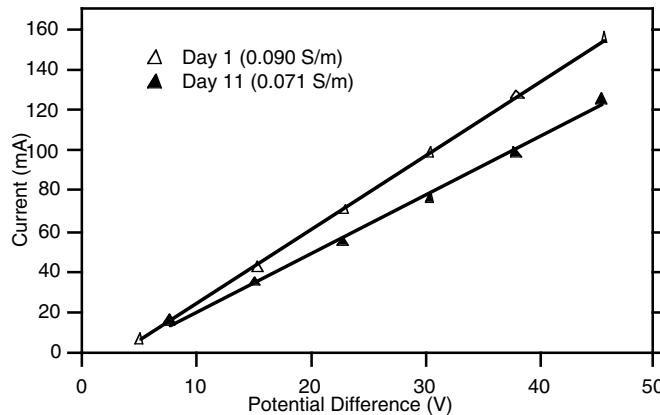

FIGURE 2. Electrical conductivity of the core is determined in the bench-top cell using Ohm's law. The current-voltage curve for the entire 15.2 cm core shows that the electrical conductivity of the core decreased during processing from 0.090 S/m at the beginning to 0.071 S/m at the end.

RESULTS AND DISCUSSION

Electrical Conductivity. In the bench-top cell, the voltage imposed between the anode and cathode (at either end of the 15.2 cm long soil core) is controlled in constant voltage mode, this voltage is referred to here as V_{14}. Further detail about the voltage drop along the core is provided by two supplemental gold hoop voltage probes at 5 and 10 cm along the core, the voltage between these probes is V_{23}. Figure 2 shows the current-voltage plots of V_{14} to be linear (V_{23}, not shown, is also linear with current). We measured a soil electrical conductivity of 0.090 S/m on day 1, decreasing to 0.071 S/m at the end of processing on day 11.

Hydraulic Conductivity. A standard technology used for remediation of organic solvent contamination at the LLNL site, "pump-and-treat", is based on pumping water through contaminated zones, extracting contaminated water, and removing the contaminants. Hydraulic flow through heterogeneous lithologies preferentially passes through sandy, permeable zones, resulting in very little penetration of clayey, fine-grained zones. It is for this reason, that we are exploring electro-osmotic pumping to specifically address the finer-grained, less permeable sediments. The core chosen for work in the bench-top cell was selected due to its high clay content, representative of the finer-grained layers in the screened zone of one of the wells. Therefore, the hydraulic conductivity measured for this core is indicative of the type of sediments we are interested in targeting for cleanup with electro-osmotic pumping, but would not be typical of a measurement between wells in a field installation.
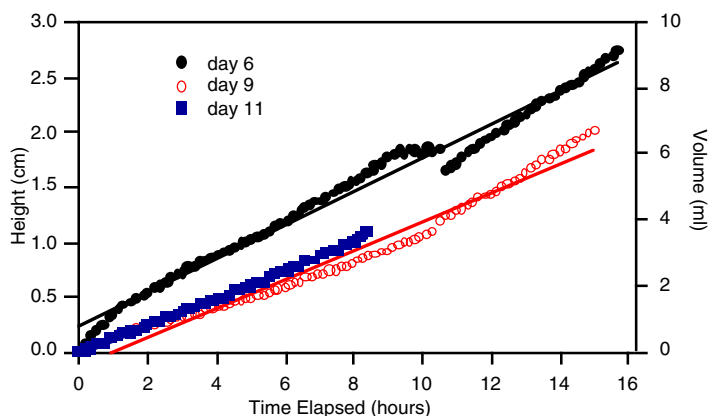

FIGURE 3. The hydraulic conductivity of the same core, measured in the bench-top cell with a 10 psi (0.069 MPa) hydraulic head gradient, shows a small decline in conductivity during electro-osmotic processing from 5.00 x 10^{-10} m/s (day 6), to 4.16 x 10^{-10} m/s (day 9), and 4.08 x 10^{-10} m/s (day 11).

Hydraulic conductivity was measured for the core in the bench-top cell using a pressure differential imposed by a pressure can, pressurized with compressed air, on the inlet side and a standpipe open to atmospheric pressure at the outlet side. Initial flow rate using a pressure gradient of 10 psi (0.069 MPa) was 0.0085 ml/min (Figure 3). This corresponds to a hydraulic conductivity for this core of $k_h = 5.00 \pm 0.36 \times 10^{-10}$ m/s. Sediments with hydraulic conductivities in this range may be considered essentially impermeable to mechanical pumping, especially when interleaving sandy layers ($k_h > 10^{-6}$ m/s) are present.

Electro-osmotic Conductivity. Electro-osmotic conductivity (k_e) measurements may be performed under controlled conditions in the bench-top cell. Five measurements taken during electro-osmotic processing are presented in Figure 4. A 3 V/cm applied voltage resulted in a q_e = 0.082 ml/min on day 3, decreasing to 0.038 ml/min on day 11. The electro-osmotic conductivity for the 3.5 inch diameter core calculated from these measurements declines from k_e = 7.37 x 10^{-10} m^2/s-V to 3.44 x 10^{-10} m^2/s-V after 11 days of processing. The sediment sample used is small, isolated from natural hydraulic gradients, and represents the finer-grained zones of a natural heterogeneous fabric.
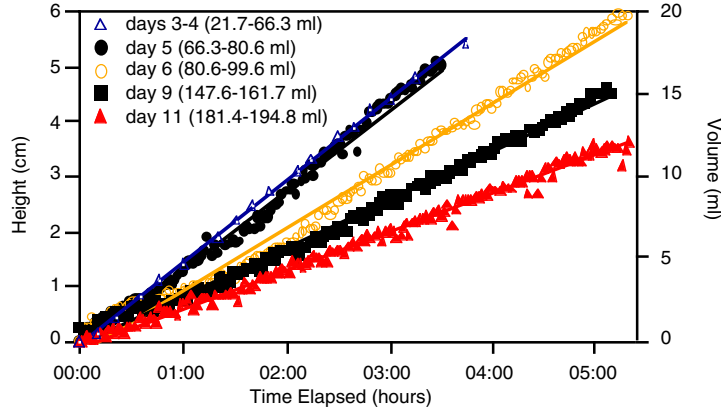

FIGURE 4. The electro-osmotic conductivity of the core, measured in the bench-top cell using a 3 V/cm voltage gradient, decreased during processing. Initially the electro-osmotic conductivity was 7.37 x 10^{-10} m^2/s-V (day 3), then 7.26 x 10^{-10} m^2/s-V (day 5), 6.11 x 10^{-10} m^2/s-V (day 6), 4.33 x 10^{-10} m^2/s-V (day 9) and 3.44 x 10^{-10} m^2/s-V (day 11).

FIGURE 5. Core at the end of electro-osmotic processing. Discoloring is seen in a zone closer to the cathode (right end), with a distinct black ring at the furthest left portion of the discolored area.

FIGURE 6. The black metals deposition and white carbonate precipitate occurred at the outer perimeter of the core, in a donut-shaped area, not evenly over the cross-sectional area of the core.
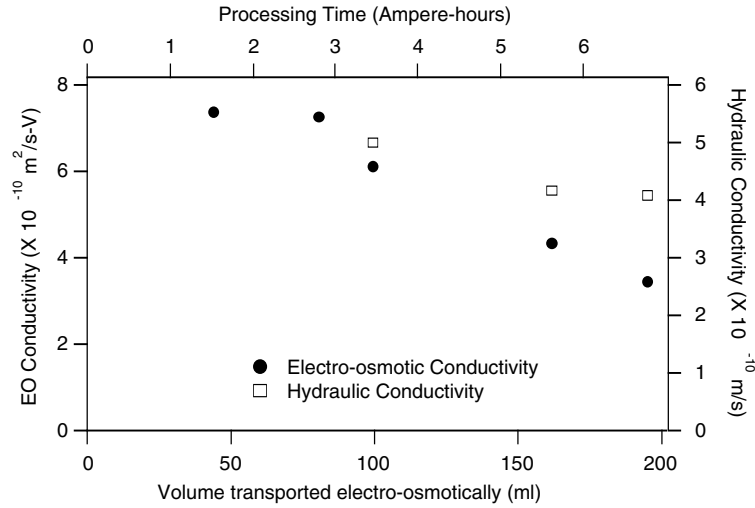
FIGURE 7. The electro-osmotic and hydraulic conductivities of the core both decreased during processing. Electro-osmotic conductivity declined by ~2x, while the decline in hydraulic conductivity was slight, ~1.2x less. The volume transported electro-osmotically, 195 ml, is 0.70 pore volumes.
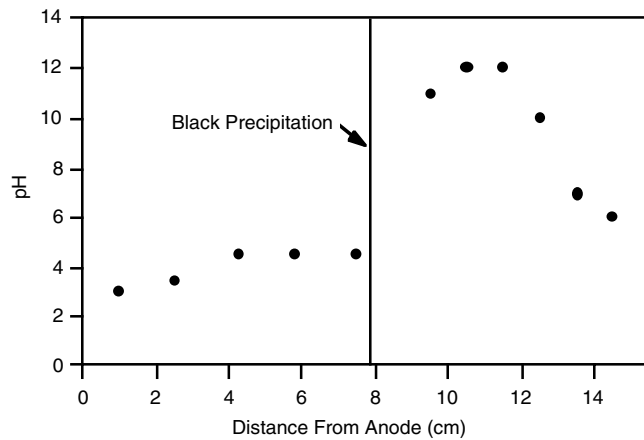

FIGURE 8. Distribution of pH along the length of the core. The anode is at the left end of the core and the cathode at the right end. The pH rises sharply at the precipitation zone.

Conclusions. We measured declines in the electrical, hydraulic and electro-osmotic conductivity of a clayey core in a bench-top test cell during electro-osmotic processing in conjunction with precipitation within the core. Metals desorbed by an acid front propagating from the anode formed a black precipitate with OH^- propagating from the cathode (Figures 5,6 and 8). In addition, where the base penetrated the core, carbonates precipitated. This precipitation zone developed closer to the cathode end, due to the lower mobility of OH^- (self-diffusion coefficient $D_0 = 52.8 \times 10^{-10}$ m^2/s) relative to H^+ ($D_0 = 93.1 \times 10^{-10}$ m^2/s) (Mitchell, 1993). Since hydraulic pumping in a heterogeneous matrix will draw water primarily through the coarse-grained zones, circumventing finer-grained zones with higher contamination, mechanical pump-and-treat technology is not effective in cleanup of sediments such as that studied in the bench-top cell. We

therefore hope to use electro-osmotic pumping to drive water through such sediments and clean up "impermeable" zones. From the initial electro-osmotic conductivity measured for the core in the bench-top experiments, 7.37×10^{-10} m^2/s-V, the "equivalent hydraulic conductivity" (k_{h-eq}) under electro-osmotic pumping (at 3 V/cm) is $k_{h-eq} = 2.21 \times 10^{-7}$ m/s. This equivalent hydraulic conductivity results in a flow through the fine-grained sediments more than 400 times greater than without the applied field ($k_h \sim 5 \times 10^{-10}$ m/s)! Electro-osmotic pumping technology offers great potential for controlled cleanup of fine-grained sediments, since flow follows the domain of the imposed electric field and passes preferentially through fine-grained sediments due to their greater electrical conductivities. It is an *in-situ* technology, requiring no excavation, nor significant chemical by-product residue. We are now testing a pH control system to minimize the formation of precipitates and we are exploring the removal efficiency of organic solvents from contaminated sediments using electro-osmotic pumping.

ACKNOWLEDGEMENTS

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